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(54) Title: RADIATION CURABLE INKJET INKS COMPOSITIONS

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right) \quad (1)$$

(57) Abstract: A non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising: (iv) a colorant (v) a photo-initiator; and (vi) a mixture of (meth)acrylate compounds; wherein: (a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and (b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

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APPLICANTS

AVECIA LIMITED

TITLE

COMPOSITIONS

COMPOSITIONS

This invention relates to radiation curable inks and to their use in ink jet printing.

Ink jet printing is a non-contact method by which droplets of ink are ejected through a fine nozzle onto a substrate. There are many demanding performance requirements for inks used in ink jet printing. For example they should provide sharp, non-feathered images having good water, solvent- light- and ozone fastness, attractive colour and high optical density. Further desirable properties for ink jet printing inks include a fast dry time (to facilitate high-speed printing), a low viscosity to enable the inks to be used in a wide range of ink jet printers, excellent mechanical resistance (to avoid the prints being rubbed off), low curl and good adhesion to a range of substrates.

Often organic solvents are included in ink jet printing inks to lower their viscosity. However such solvents can give rise to undesirable odours, particularly in the home and small, poorly ventilated offices. Inclusion of low boiling point organic solvents should be avoided in order to minimise the release of volatile organic solvents into the atmosphere. Inclusion of high boiling point solvents can increase ink dry times significantly.

US 5,270,368 discloses radiation-curable etch-resistant compositions for ink jet printing containing large proportions of monofunctional and difunctional monomers in combination with large amounts of organic solvents such as methanol to achieve a sufficiently low viscosity for jetting.

US 4,303,924 discloses radiation curable ink jet printing inks containing organic solvent and large proportions of trifunctional monomers.

WO 02/38688 discloses low viscosity radiation curable compositions which are free from solvent and have low proportions of difunctional and tri- or higher functional monomers.

According to the first aspect of the present invention there is provided a non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising:

(i) a colorant

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more

(meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1).

Preferably the value of Formula (1) is from 40 to 60, more preferably from 42.6 to 57, especially from 49 to 55.8.

The amount of colorant in the ink is preferably from 0.1 to 14%, more preferably from 1 to 10% and especially from 1.1 to 8% by weight, relative to the total weight of the ink. Preferably the colorant is not white. Preferred colorants are yellow, magenta, cyan, black, blue, indigo, violet, green, orange, red and mixtures comprising two or more thereof. Preferably the ink is free from titanium dioxide.

The colorant is preferably a dye, a pigment or a mixture thereof. More preferably the colorant is a pigment. Preferred dyes and pigments are free from ionic groups, for example disperse dyes and water-insoluble pigments are especially preferred colorants. Preferred pigments are organic or inorganic. The pigment is preferably in the form particles which are small enough to pass through the very fine nozzles used in the printheads of ink jet printers. Typically these nozzles are half the diameter of a human hair. Thus the average particle size of the pigment is preferably from 0.003 to 15 μm, more preferably from 0.004 to 5 μm and especially from 0.005 to 1μm. By choosing particles of this size advantages can be achieved in terms of storage stability for the ink and high optical density for the resultant prints. Pigment particle sizes outside these ranges may be used where printheads have particularly large nozzle diameters. Very fine dispersions of pigments and methods for their preparation are disclosed in, for example, EP 0 776 952, US 5,538,548, US 5,443,628, EP 0 259 130, US 5,285,064, EP 0 429 828 and EP 0 526 198.

Examples of inorganic pigments include carbon black, titania, iron oxide, zinc oxide and mixtures thereof. Examples of organic pigments include phthalocyanines, anthraquinones, perylenes, carbazole, monoazo and disazobenzimidazolones, isoindolinones, monoazonaphthols, diarylidepyrazolones, rhodamines, indigoids, quinacridones, diazopyranthrones, dinitranilines, pyrazolones, dianisidines, pyranthrones, tetrachloroisoindolinones, dioxazines, monoazo acrylides, anthrapyrimidines and mixtures thereof.

Examples of carbon black pigments include Regal 400R, Mogul™ L, Elftex™ 320 from Cabot Co., or Carbon Black FW18, Special Black 250, Special Black 350, Special Black 550, Printex™ 25, Printex™ 35, Printex™ 55 and Printex™ 150T from Degussa Co., and Pigment Black 7.

Further examples of pigments include C.I. Pigment Yellow 17, C.I. Pigment Blue 27. C.I. Pigment Red 49:2, C.I. Pigment Red 81:1, C.I. Pigment Red 81:3, C.I. Pigment Red 81:x, C.I. Pigment Yellow 83, C.I. Pigment Red 57:1, C.I. Pigment Red 49:1, C.I. Pigment Violet 23, C.I. Pigment Green 7, C.I. Pigment Blue 61, C.I. Pigment Red 48:1, C.I. Pigment Red 52:1, C.I. Pigment Violet 1, C.I. Pigment White 6, C.I. Pigment Blue 15, C.I. Pigment Yellow 12, C.I. Pigment Blue 56, C.I. Pigment Orange 5, C.I. Pigment Black 7, C.I. Pigment Yellow 14, C.I. Pigment Red 48:2, C.I. Pigment Blue 15:3, C.I. Pigment Yellow 1, C.I. Pigment Yellow 3, C.I. Pigment Yellow 13, C.I. Pigment Orange 16, C.I. Pigment Yellow 55, C.I. Pigment Red 41, C.I. Pigment Orange 34, C.I. Pigment Blue 62, C.I. Pigment Red 22, C.I. Pigment Red 170, C.I. Pigment Red 88, C.I. Pigment Yellow 151, C.I. Pigment Red 184, C.I. Pigment Blue 1:2, C.I. Pigment Red 3, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Red 23, C.I. Pigment Red 112, C.I. Pigment Yellow 126, C.I. Pigment Red 169, C.I. Pigment Orange 13, C.I. Pigment Red 1-10, 12, C.I. Pigment Blue 1:X, C.I. Pigment Yellow 42, C.I. Pigment Red 101, C.I. Pigment Brown 6, C.I. Pigment Brown 7, C.I. Pigment Brown 7:X, C.I. Pigment Black 11, C.I. Pigment Metal 1, C.I. Pigment Metal 2, C.I. Pigment Yellow 128, C.I. Pigment Yellow 93, C.I. Pigment Yellow 74, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 154, C.I. Pigment Yellow 185, C.I. Pigment Yellow 180, C.I. Pigment Red 122, C.I. Pigment Red 184, and bridged aluminium phthalocyanine pigments.

Further pigments are listed in *The Colour Index* and updates thereof, especially the 3rd edition, 1982, pages 6-146.

The especially preferred pigments are Pigment Yellow 128, 93, 17, 74, 138, 139, 154, 185, 180; Pigment Red 122, 57:1, 184; Pigment Blue 15:3, 15:4 and carbon black.

Preferred dyes include azo, diazo, xanthene, anthraquinone, triaryl methane, azine, thiazine, phthalocyanine and nigrosine types. Dyes may be used singly or in combination with other dyes and/or pigments. Dyes are preferably disperse or solvent soluble, examples of which may be selected from *The Colour Index* especially the 3rd edition, 1982, pages 147-263. Dyes can be metalised or non-metalised.

The ink optionally further contains a dispersant. When the colorant is a disperse dye a dispersant is often not necessary because the dye may be soluble in the formulation. Similarly when the pigment is self-dispersible (e.g. the pigment carries dispersing groups or is surface modified to be self-dispersible) no further dispersant is needed. However when the colorant is insoluble in the mixture of (meth)acrylate compounds (component (iii)) a dispersant is preferably included in the ink to assist storage stability. Suitable dispersants include, for example, polyester, polyurethane and polyacrylate dispersants, especially those in the form of high molecular weight block copolymer. Examples of dispersants include Disperbyk™ (ex BYK Chemie) and Solsperse™ (ex Avecia) dispersants. A detailed list of non-polymeric as well as some polymeric dispersants appears in, for example, *McCutcheon's Functional Materials,* North

American Edition, Manufacturing Confectioner Publishing Co., Glen Rock, N.J., pp.110-129 (1990), the entire disclosure of which is incorporated herein by reference. Dispersants suitable for use with pigments are also disclosed in DE 19636382, US 5,720,802, US 5,713,993, PCT/GB95/02501, US 5,085,689 and GB 2303376. When the ink contains a dispersant this is preferably present in an amount of 50 to 150% by weight relative to the weight of colorant.

Examples of self-dispersing pigments include surface treated carbon blacks carrying carboxy, sulphonate and/or ethylene oxide groups.

The pigment and dispersant are preferably added to the ink as a mixture. For example, a mixture of a pigment and a dispersant may be made by milling pigment in a small amount of the (meth)acrylate components c), d) and e) with a milling media, e.g. glass beads. The pigment dispersion is then typically screened and "let down" by slowly adding the remaining ink components.

The amount of photo-initiator in the ink is preferably 0.1 to 15%, more preferably 3 to 12% by weight, relative to the total weight of the ink. Preferred photo-initiators include alpha diketones, monoketals of alpha-diketones or ketoaldehydes, acyloins and their corresponding ethers, chromophore-substituted halo-s-triazines, and chromophore-substituted halomethyl-oxadiozoles. Specific examples of photo-initiators include acetophenone, propiophenone, 2-phenyl-acetophenone, 2-chloro-2-phenyl-acetophenone, 2-2-dichloro-2-phenyl-acetophenone, 2-butoxy-2-phenyl acetophenone, 2,2-dimethoxy-2-phenyl-acetophenone, 2,2-diethoxy-acetophenone, 2-methylol-2-methoxy-2-phenyl-acetophenone, benzophenone, 4-trichloromethyl benzophenone, indenone, 1-3-indanedione, fluorenone, xanthone, thioxanthone, 2-chlorothioxanthone, anthraquinone, 2-ethylanthraquinone, biacetyl, glyoxal, 1,2-indanedione, p-chlorophenyl-glyoxal, benzil, camphoquinone, and benzoin methyl and ethyl esters. Commercial photo-initiators particularly suitable for use in the present invention include Speedcure™ ITX, and Irgacure™ 369. The ink optionally further contains one or more co-initiators or amine synergists in order to improve cure rate. Examples include isopropylthioxanthone, ethyl-4-(dimethylamine) benzoate, 2-ethyl hexyl dimethylaminobenzoate and dimethylaminoethyl methacrylate.

Preferably the photo-initiator is other than a cationic photo-initiator. Preferably the photo-initiator is a free radical photo-initiator.

Preferably the photo-initiator is soluble in the ink.

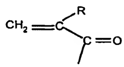
A single photo-initiator may be used although it is preferable that the photo-initiator is a mixture of two or more photo-initiators because this can lead to a broader spectral response, improved depth of cure and improved cure rate with opacifying pigments such as carbon black.

Preferably the ink further comprises a stabiliser to improve the storage stability of the ink and prevent premature curing. The stabiliser is preferably an antioxidant, a radical trap, a radical quencher or the like, e.g. a phenol, thiol, quinone, hydroquinone, amine,

xanthate or an N-alkyl or N-aryl aniline. Too much stabiliser will prevent cure entirely. Hence preferred amounts of stabiliser are from 0 to 10%, more preferably from 0.01 to 5%, and especially from 0.1 to 3% by weight relative to the total weight of the ink. Mixtures of stabilisers are preferable for the best ink storage lifetime.

Preferably the ink is curable by actinic radiation or particle beam, especially by UV or electron beam radiation.

Mono (meth)acrylate compounds have one (and only one) acrylate or methacrylate group. This group is, as is known in the art, is polymerisable when irradiated in the presence of a photo-initiator. (Meth)acrylate groups are represented by the formula:



wherein R is H or methyl

The mono (meth)acrylate compound is preferably a monomer. Examples mono (meth)acrylate monomers include cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl (meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate. Preferred mono (meth)acrylate monomers include lauryl (meth)acrylate, tetrahydro furfuryl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, iso-octyl (meth)acrylate, iso-decyl (meth)acrylate, tridecyl (meth)acrylate, dodecyl (meth)acrylate, isobornyl (meth)acrylate, cyclic trimethylol propane formal (meth)acrylate.

It is especially preferred that the one or more monomer (meth)acrylate compounds is or comprises isobornyl acrylate.

Di (meth)acrylate compounds have two (and only two) groups selected from acrylate and methacrylate.

Preferred di (meth)acrylate compounds are di (meth)acrylate monomers, for example di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy

ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol.

It is especially preferred that the one or more di(meth)acrylate compounds is or comprises 1,6 hexane diol diacrylate.

The compound(s) having three or more (meth) acrylate groups have three or more groups selected from acrylate and methacrylate. The compound having three or more (meth)acrylate groups is preferably a monomer, oligomer or polymer, preferred examples of which include trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics.

It is especially preferred that the one or more compounds comprising three or more (meth)acrylate groups is or comprises trimethylol propane triacrylate and/or ethoxylated trimethylol propane triacrylate.

Inks which contain acrylates polymerise more quickly than those containing methacrylates when exposed to actinic or particle beam radiation. Consequently, the amount of methacrylate is preferably not greater than 20%, more preferably not greater than 10% and especially not greater than 5% of component (iii). It is particularly preferred that component (iii) contains no methacrylate.

Optionally the ink further comprises a polymer or oligomer containing no (meth)acrylate groups. Preferably the polymer and oligomer containing no (meth)acrylate groups is present in the ink at from 0 to15%, more preferably from 0 to 10% and most preferably from 0 to 5% by weight relative to the total weight of the ink.

Inks of the present invention are substantially solvent free. That is to say no solvent or water is present in the ink except for trace amounts which may be present as impurities in any of the ink components. Preferably any such residues are less than 2%, more preferably less than 0.5% and especially less than 0.01% by weight relative to the total weight of ink. As hereinbefore described inks of the present invention are particularly suitable for use in ink jet printing. A preferred ink jet type for inks of the present invention is piezo ink jet printing.

The viscosity of the inks of the present invention are preferably 1 to 30 mPa.s, more preferably from 2 to 25 mPa.s at 60°C. The ink composition may optionally have a higher viscosity at room temperature provided that the final ink meets the above viscosity requirements at the above temperature.

The surface tension of the ink of the present invention is preferably below 40 dynes/cm.

Inks of the present invention are preferably free from particulate impurities that would tend to block an ink jet nozzle. To achieve this the ink is preferably filtered through a filter with a pore size of less than 10μm, more preferably less than 3μm and especially less than 1μm.

A particularly preferred ink according to the invention is a non-aqueous, substantially solvent-free, radiation curable ink having a viscosity of 1 to 30m Pa.s at 60°C comprising:

(i) a yellow, magenta, cyan, black, blue, indigo, violet, green, orange or red pigment or a mixture comprising two or more thereof;

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the pigment is present in the ink an amount of from 1.1 to 8% by weight relative to the total weight of ink;

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is from 40 to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1)

(c) the photo-initiator is present in the ink in an amount of 3 to 12% by weight relative to the total weight of ink;

(d) the one or more mono (meth)acrylate compounds are selected from the group consisting of cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl

(meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate and mixtures thereof;

(e) the one or more di (meth)acrylate compounds are selected from the group consisting of di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol and mixtures thereof; and

(f) the one or more compounds having three or more (meth)acrylate groups are selected from the group consisting of trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics and mixtures thereof.

In this preferred ink the mixture of (meth)acrylate compounds is preferably present in the ink in an amount of from 70 to 95.9%, more preferably from 75 to 95.9%, and especially from 78 to 95.9% by weight relative to the total weight of ink. Any difference between the weight of components (i), (ii) and (iii) and 100% is made up by other customary ink additives, e.g. flow control agents, dispersants, biocides, rheology modifiers and so on other than water or organic solvent.

Inks of the present invention may contain further components in addition to components (i) to (iii) specified above, for example preservatives, biocides, rheology modifiers, surfactants, levelling agents, antifoaming agents, anti-kogation agents and combinations thereof.

According to a second aspect of the present invention there is provided a process for printing an image onto a substrate comprising applying thereto an ink according to the first aspect of the present invention by means of an ink jet printer and curing the ink, preferably using an electron beam or more preferably using ultra violet light. Printed substrates obtained by this process form a further feature of the present invention.

Preferred substrates are metal, plastic, ceramic, glass, wood, printed circuit boards and plain and coated papers. Preferred applications include printing for home/office use, packaging, labelling and barcodes, particularly wide format graphics, printed circuit board manufacture, signage, wall coverings and decorative laminates.

According to a third aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and an ink wherein the ink is present in the chamber and is as defined in the first aspect of the invention.

The invention in further illustrated by the following examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

A radiation curable ink was prepared containing the following components:

Component	Weight (g)	Type
Sartomer™ 256	10.02	Monoacrylate
Sartomer™ 238	10.02	Diacrylate
Sartomer™ 351	40.07	Triacrylate
Regal ™ 250R	1.75	Pigment
Solsperse™ 32000	1.09	Dispersant
Solsperse™ 5000	0.06	Dispersant
Irgacure™ 369	2.80	Photo-initiator
Speedcure™ EHA	2.80	Amine Synergist
Speedcure™ ITX	1.40	Photo-initiator

The procedure for preparation of the above ink was as follows:

A millbase was prepared by bead milling Regal™ 250R pigment with a small amount of Sartomer™ 256 and Sartomer™ 238 together with Solsperse™ 32000 and 5000 dispersants until a fine particle dispersion was formed. The remaining components were then added in the dark and the mixture was homogenised and then filtered through a 1 micron Whatman™ syringe filter.

The percentages of mono acrylate (16.7%), di acrylate (16.7%) and tri acrylate (66.6%) compounds by weight relative to the total weight of such compounds (100%) are such that the value of Formula (1) was (16.7 + 0.628 X (16.7/sin 60 + 66.6/tan60) = 52.93.

Comparative Example 1

A radiation curable ink was prepared (in an analogous manner to Example 1) containing the following components:

Component	Weight (g)	Type
Sartomer™ 256	39.55	Monoacrylate
Sartomer™ 238	9.89	Diacrylate
Sartomer™ 351	9.89	Triacrylate
Regal™ 250R	1.73	Pigment
Solsperse™ 32000	1.08	Dispersant
Solsperse™ 5000	0.06	Dispersant
Irgacure™ 369	2.76	Photo-initiator
Speedcure™ EHA	2.76	Amine Synergist
Speedcure™ ITX	1.38	Photo-initiator

The percentages of mono acrylate , di acrylate and tri acrylate compounds by weight relative to the total weight of such compounds are such that the value of Formula (1) was 84.79.

Results

The inks describe in Example 1 and Comparative Example 1 were each coated onto sheen cards using an 8μm K-bar coater. The coatings were cured using Fusion Systems apparatus fitted with a "D" 300W/inch bulb using cure energy in the range UV_A 0.37 – 0.74, UV_B 0.172 – 0.99 and UV_C 0.07 – 0.11 at belt/cure speeds of 25M/min or 15M/min.

The Reflectance Optical Density (ROD) of the cured coated sheen cards was measured using an XRite 938 Spectrodensitometer using density status T, illuminant D50 and 2° observer.

The Chemical Resistance (% loss) was determined by performing 5 x MEK (methyl ethyl ketone) double rubs on the coated cured sheen cards and then measuring the ROD in the rubbed region. The Chemical Resistance (% loss) value was then expressed via

$$\text{Chemical Resistance (\% loss)} = 100\ \frac{(\text{ROD Initial} - \text{ROD after 5 x MEK rubs})}{\text{ROD Initial}}$$

Hence small values of Chemical Resistance (% loss) represent higher solvent resistance.

The viscosity was measured by using a Brookfield viscometer at 50°C operating at 100 revolutions per minute and using a UL spindle

The surface tension of the inks were determined at 25°C using a Kruss Surface Tension Balance.

The hardness of the print was assessed in the conventional manner using pencils of different hardness, where the hardness is determined as the lowest hardness value that forms a scratch in the print.

Property	Example 1	Comparative Example 1
ROD	1.821	1.668
Chemical Resistance (% loss)	1.7	29.2
Viscosity (@ 50°C) mPa.s	11.5	4.32
Surface Tension (@ 25°C) dynes/cm	37	37
Pencil Hardness	4H	6B
Belt Cure Speed	25	15

The above table shows that the ink of Example 1 has better chemical resistance and a faster cure speed than Comparative Example 1 whilst still retaining a low viscosity suitable for ink jet printing. Furthermore, Example 1 has better pencil hardness and a higher ROD than Comparative Example 1. The ink described in Example 1 was readily jetted through a Spectra Galaxy printhead.

Further inks of the present invention were prepared (in an analogous manner to Example 1) containing:

Ingredient		Yellow %	Magenta %	Cyan %	Black %
Sartomer™ 506	Isobornyl acrylate	8.73	8.18	8.58	8.57
Sartomer™ SR238	1,6 hexanediol diacrylate	22.48	30.84	25.42	22.74
Sartomer™ 306	tripropyleneglycol diacrylate	3.7	5.95	2.97	4.18
Sartomer™ SR351	trimethylolpropane triacrylate	34.9	24.53	32.54	33.48
Sartomer™ SR454	Ethoxylated trimethylolpropane triacrylate	17.45	12.26	16.28	16.74
Tegorad™ 2100	ST modifier (silicone acrylate)	0.15	0.15	0.15	0.15
Irgacure™ 369	Photo-initiator	4	4	4	4
Speedcure™ EHA	Amine Synergist	4	4	4	4
Speedcure™ ITX	Photo-initiator	2	2	2	2
Paliotol™ Yellow D1819	Pigment	2	0	0	0
Hostaperm™ Red E5B02	Pigment	0	5	0	0
Irgalite™ Blue GLVO	Pigment	0	0	2.5	0
Regal™ 250	Pigment	0	0	0	2.5
Solsperse™ 32000	Dispersant	0.6	3	1.5	1.56
Solsperse™ 5000	Dispersant	0	0.1	0.05	0.09

Such inks showed excellent printing performance through a Spectra Galaxy printhead and had very good chemical resistance.

CLAIMS

1. A non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising:

   (i) a colorant
   (ii) a photo-initiator; and
   (iii) a mixture of (meth)acrylate compounds;

wherein:

   (a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and
   (b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1).

2. An ink according to claim 1 wherein the colorant is a pigment.

3. An ink according to any one of the preceding claims wherein the mono (meth)acrylate compounds and di (meth)acrylate compounds are monomers.

4. An ink according to any one of the preceding claims wherein the value of Formula (1) is from 49 to 55.8.

5. An ink according to any one of the preceding claims wherein the photo-initiator is a free radical photo-initiator.

6. An ink according to any one of the preceding claims wherein the one or more mono (meth)acrylate compounds is or comprises isobornyl acrylate.

7. An ink according to any one of the preceding claims wherein the one or more di (meth)acrylate compounds is or comprises 1,6 hexanediol diacrylate.

8. An ink according to any one of the preceding claims wherein the one or more compound comprising three or more (meth)acrylate groups is or comprises trimethylolpropane triacrylate and/or ethoxylated trimethylolpropane triacrylate.

9. An ink according to any one of the preceding claims which further comprises a dispersant and/or an amine synergist.

10. An ink according to any one of the preceding claims wherein the colorant is present in an amount of 1.1 to 8% by weight, relative to the total weight of the ink.

11. An ink according to any one of the preceding claims wherein the colorant is not white.

12. An ink according to any one of the preceding claims which is free from titanium dioxide.

13. An ink according to any one of the preceding claims wherein the photo-initiator is present in an amount of 3 to 12 % by weight, relative to the total weight of the ink.

14. An ink according to claim 1 comprising:

- (i) a yellow, magenta, cyan, black, blue, indigo, violet, green, orange or red pigment or a mixture comprising two or more thereof;
- (ii) a photo-initiator; and
- (iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the pigment is present in the ink an amount of from 1.1 to 8% by weight relative to the total weight of ink;

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is from 40 to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1)

(c) the photo-initiator is present in the ink in an amount of 3 to 12% by weight relative to the total weight of ink;

(d) the one or more mono (meth)acrylate compounds are selected from the group consisting of cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl (meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate and mixtures thereof;

(e) the one or more di (meth)acrylate compounds are selected from the group consisting of di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol and mixtures thereof; and

(f) the one or more compounds having three or more (meth)acrylate groups are selected from the group consisting of trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics and mixtures thereof.

15. An ink according to any one of the preceding claims which has been filtered through a filter having a mean pore size of less than 10μm.

16. An ink according to any one of the preceding claims for use in ink jet printing.

17. A process for printing an image onto a substrate comprising printing an image onto a substrate using an ink according to any one of the preceding claims by means of an ink jet printer and curing the ink.

18. A process according to claim 17 wherein the curing is performed using an electron beam or ultra violet light.

19. A printed substrate obtained by the process of claim 17 or 18.

20. An ink jet printer cartridge comprising a chamber and an ink wherein the ink is present in the chamber and is as defined in one of claims 1 to 16.

21. A substrate printed with an image using an ink according to any one of the claims 1 to 16.

22. A substrate printed with an image by a process according to claim 17 or 18.

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Int[redacted]ional Application No
PCT/GB 03/03836

A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 29788 A (JOHNSON STEVE ;XAAR TECH LTD (GB); WOODS JILL (GB)) 17 June 1999 (1999-06-17) page 3, paragraph 1 -page 4, paragraph 1 page 5, paragraph 4 -page 8, paragraph 3 page 9, paragraph 2 -page 12, paragraph 1 page 16, paragraph 1 -page 17, line 7 page 17, paragraph 2 -page 18, paragraph 1 page 21, paragraph 2; examples 1,2 ---	1-22
P,X	EP 1 323 795 A (UCB SA) 2 July 2003 (2003-07-02) paragraphs '0014!-'0020!; table 1 ---	1-22
X	US 6 114 406 A (CAIGER NIGEL ANTONY ET AL) 5 September 2000 (2000-09-05) column 2, line 13-67 column 3, line 1-8; examples 1-5 ---	1-13, 17-22

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[X] Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 29787 A (JOHNSON STEVE ;XAAR TECH LTD (GB); WOODS JILL (GB)) 17 June 1999 (1999-06-17) page 3, paragraphs 1,2 page 5, paragraph 3 -page 8, line 3 page 8, paragraph 2 -page 11, paragraph 1 page 15, paragraph 2 -page 17, paragraph 1 page 17, paragraph 3 -page 18, paragraph 1 page 19, paragraph 2 page 21, paragraph 3; table 1 ---	1-10, 13-22
X	US 5 275 646 A (HUDD ALAN L ET AL) 4 January 1994 (1994-01-04) column 1, line 24-27 column 3, line 23-31 column 3, line 45-55 column 3, line 61-65 column 4, line 5-19 column 4, line 36-43 column 5, line 11-31; claim 10; examples 1,2 -----	1-8, 10-13, 17-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 03/03836

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9929788 A	17-06-1999	AU 1346399 A	28-06-1999
		GB 2346889 A ,B	23-08-2000
		WO 9929788 A1	17-06-1999
EP 1323795 A	02-07-2003	EP 1323795 A1	02-07-2003
		WO 03054091 A1	03-07-2003
US 6114406 A	05-09-2000	AU 1804597 A	10-09-1997
		DE 69700697 D1	02-12-1999
		DE 69700697 T2	08-06-2000
		EP 0882104 A1	09-12-1998
		WO 9731071 A1	28-08-1997
		JP 2000504778 T	18-04-2000
WO 9929787 A	17-06-1999	AU 1346299 A	28-06-1999
		BR 9813371 A	24-09-2002
		CA 2310633 A1	17-06-1999
		CN 1301284 T	27-06-2001
		EP 1034228 A2	13-09-2000
		WO 9929787 A2	17-06-1999
		JP 2001525479 T	11-12-2001
		US 6593390 B1	15-07-2003
US 5275646 A	04-01-1994	DE 69106952 D1	09-03-1995
		DE 69106952 T2	24-05-1995
		EP 0465039 A1	08-01-1992
		JP 3189012 B2	16-07-2001
		JP 5214279 A	24-08-1993
		DE 69215835 D1	23-01-1997
		DE 69215835 T2	03-04-1997
		EP 0540203 A1	05-05-1993
		JP 5214280 A	24-08-1993

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(54) Title: RADIATION CURABLE INK JET INK COMPOSITIONS

(57) Abstract

A radiation curable ink jet ink having a viscosity not greater than 35 mPa.s at 30 °C and comprising a colorant component, a diluent consisting essentially of reactive liquid material and, optionally, at least one photopolymerisation catalyst and wherein the reactive liquid material is formed of both monofunctional and polyfunctional material and comprises 5 to 30 % by weight of at least one oligomer.

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RADIATION CURABLE INK JET INK COMPOSITIONS

This invention relates to ink jet ink compositions and in particular to such compositions which are curable by ultra-violet radiation.

Radiation curable inks e.g. for screen printing and offset printing have been known for some time and more recently, there have been proposals for radiation-curable ink jet inks; see, for example, GB-A-2233928, JP-A-63102936, US-A-4303924, EP-A-0540203, EP-A-0465039 and WO97/31071. There are, however, substantial problems in arriving at a radiation-curable formulation which meets all the criteria required of an ink jet ink; specifically, low viscosity, the required level of surface tension, low volatility, long term stability, rapid drying of the ink dot derived from the droplet ejected from the nozzle of the print head, and the provision of print of satisfactory quality, especially resistance to scratching and adhesion to the substrate.

We have now developed a radiation curable ink jet ink which is essentially free of non-reactive diluent and yet has the desired viscosity, surface tension, volatility, stability and drying rate and produces print of acceptable quality. Inks according to the invention thus can be printed without difficulty from ink jet printers to give good quality print on a variety of substrates including such disparate materials as paper and non-adsorbent materials e.g. metal. They are of particular interest, however, in printing on plastics which are difficult to print on, e.g. polyolefins

such as polyethylene and polypropylene.

According to one aspect of the present invention, there is provided a radiation curable ink jet ink having a viscosity not greater than 35 mPa.s at 30°C as measured using a Brookfield Viscometer fitted with a small sample adaptor having a No. 18 spindle and at a rotational speed of 60 rpm, giving a shear rate of 79.2 sec^{-1}, and comprising a colorant component, a diluent consisting essentially of reactive liquid material and, optionally, at least one photopolymerisation catalyst and wherein the reactive liquid material is formed of both monofunctional and polyfunctional material and comprises from 5 to 30% by weight of at least one oligomer.

By consisting essentially of reactive liquid material, we mean that the diluent is free or substantially free of non-reactive components; that is to say, if any non-reactive liquid component is present in the diluent it forms no more than 1% by weight of the ink, preferably not more than 0.5%, by weight.

By reactive material we mean material containing one or more unsaturated carbon-carbon bonds polymerisable by radiation. In accordance with the invention, the reactive material comprises a mixture of monomer and oligomer. Oligomer is sometimes known as prepolymer. Non-limiting examples of monomers are acrylates, methacrylates and

alkoxylated and polyalkoxylated derivatives thereof. Non-limiting examples of oligomers (prepolymers) are polyester-, urethane- and epoxy-acrylates.

Preferably, said at least one oligomer has an equivalent weight of at least 180. Print obtained from inks containing oligomer exhibits improved toughness, adhesion and/or scratch resistance as compared with print derived from the same ink composition but excluding oligomer.

Preferably, the oligomer is liquid so as to maintain the desired low viscosity of the ink and preferably it has a functionality greater than 1. If it is not liquid, it should be soluble in the liquid components of the reactive material. In any event, the oligomer is deemed to form part of the reactive liquid material.

In another preferred embodiment, the ink composition includes a silicone derivative containing carbon-carbon unsaturation which is polymerisable by radiation, to adjust the surface tension of the ink. This polymerisable silicone derivative, if present, is also deemed to form part of the reactive liquid material.

While the possibility of formulating the compositions of the invention to be cured using other radiation sources, e.g. electron beam, is not excluded, the compositions are preferably formulated to be curable by visible, or more

preferably ultra violet, light, in which case they will usually include at least one photoinitiator.

The components of the compositions of the invention will now be described in greater detail.

The colorant is preferably thermally stable and water-insoluble. While the possibility of using colorants such as dyes, which are soluble in the diluent is not excluded, it is preferred to use those, such as pigments, which are insoluble, especially where light-fastness is important. In this case, it may be desirable to include a dispersant in the composition to stabilise the dispersion of insoluble colorant in the diluent.

Examples of insoluble colorants include, in particular, carbon black and those colorants characterised as pigment dyes in The Colour Index.

Examples of suitable pigments include those within the ranges having the following CI classifications:

Colour	CI Number
Green	PG 7 and 36
Orange	PO 5, 34, 36, 38, 43, 51, 60, 62, 64, 66, 67 and 73
Red	PR 112, 149, 170, 178, 179, 185,

	187, 188, 207, 208, 214, 220, 224, 242, 251, 254, 255, 260 and 264
Magenta/Violet	PV 19, 23, 31, and 37 and PR 122, 181 and 202
Yellow	PY 17, 120, 138, 155, 168, 175, 179, 180, 181 and 185
Blue	PB 15
Black	PB 2, 5 and 7.

Examples of specific pigments include IRGALITE BLUE GLVO, MONASTRAL BLUE FGX, IRGALITE BLUE GLSM, HELIOGEN BLUE L7101F, LUTETIA CYANINE ENJ, HELIOGEN BLUE L6700F, MONASTRAL GNXC, MONASTRAL GBX, MONASTRAL GLX, MONASTRAL 6Y, IRGAZIN DPP ORANGE RA, NOVAPERM ORANGE H5G70, NOVPERM ORANGE HL, MONOLITE ORANGE 2R, NOVAPERM RED HFG, HOSTAPERM ORANGE HGL, PALIOGEN ORANGE L2640, SICOFAST ORANGE 2953, IRGAZIN ORANGE 3GL, CHROMOPTHAL ORANGE GP, HOSTAPERM ORANGE GR, PV CARMINE HF4C, NOVAPERM RED F3RK 70, MONOLITE RED BR, IRGAZIN DPP RUBINE TR, IRGAZIN DPP SCARLET EK, RT-390-D SCARLET, RT-280-D RED, NOVAPERM RED HF4B, NOVAPERM RED HF3S, NOVAPERM RD HF2B, VYNAMON RED 3BFW, CHROMOPTHAL RED G, VYNAMON SCARLET 3Y, PALIOGEN RED L3585, NOVAPERM RED BL, PALIOGEN RED 3880 HD, HOSTAPERM P2GL, HOSTAPERM RED P3GL, HOSTAPERM RED E5B 02, SICOFAST RED L3550, SUNFAST MAGENTA 122, SUNFAST RED 122, SUNFAST VIOLET 19 228-0594, SUNFAST VIOLET 19 228-1220, CINQUASIA VIOLET RT-791-D, VIOLET R NRT-201-D, RED B NRT-796-D, VIOLET R RT-101-D, MONOLITE

VIOLET 31, SUNFAST MAGENTA 22, MAGENTA RT-243-D, MAGENTA RT 355-D, RED B RT-195-D, CINQUASIA CARBERNET RT-385-D, MONOLITE VIOLET R, MICROSOL VIOLET R, CHROMOPTHAL VIOLET B, ORACET PINK RF, IRGALITE YELLOW 2GP, IRGALITE YELLOW WGP, PV FAST YELLOW HG, PV FAST YELLOW H3R, HOSTAPERM YELLOW H6G, PV FAST YELLOW, PALIOTOL YELLOW D1155 and IRGAZIN YELLOW 3R.

Mixtures of colorants may be employed, if desired, including mixtures of dyes, mixtures of pigments and mixtures of one or more dyes with one or more pigments.

In one preferred embodiment of the invention, the colorants are chosen to give the widest range of colours and tones in a hexachrome system.

The amount of colorant employed in the ink will depend on the choice of colorant and the depth of colour required in the print, and can be established by simple experiment. In general, for pigments it will fall within the range 0.01% to 50% by weight, the amount chosen being such that viscosity of the ink does not exceed 35 mPa.s. For organic pigments the amount will generally be in the range 0.01 to 10% weight, more preferably 0.05 to 6%, most preferably 0.05 to 3%.

Where the colorant comprises a pigment which is to be dispersed in the diluent, it preferably has a particle size

of not greater than 1μm maximum dimension and more preferably not greater than 0.5μm. Even more preferably, the particles have a narrow size range distribution.

Where the ink comprises a dispersion of pigment, a dispersant will normally be required to aid or stabilise the dispersion. The choice of dispersant will depend upon the nature of the pigment and composition of the diluent. Examples of suitable materials may be found amongst dispersants sold under the trade names of Solsperse, EFKA and Byk. Mixtures of dispersants and mixtures of one or more dispersants with one or more dispersant synergists may be employed. The amount of dispersant employed (or dispersant and synergist where used) will depend upon the choice and concentration of the pigment. For organic pigments, the amount will usually be in the range 15 to 100% by weight of the pigment, preferably 20 to 75% by weight. For inorganic pigments, lower concentrations may be acceptable, e.g. 5% or less.

The reactive liquid material of the ink composition comprises both monofunctional and difunctional material. Preferably, it includes monofunctional, difunctional and tri- or higher functional material. By mono-, di-, tri- and higher functional material is meant compounds having, respectively, one, two, three or more unsaturated carbon-carbon groups which are polymerisable by radiation, especially but not exclusively ultra-violet light.

Examples of some suitable compounds may be found in the publication U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints, edited by R. Holman and published by SITA-Technology, London, in 1984 and The Printing Ink Manual, Fourth Edition, published by VNR International, However, the choice of suitable compound is not limited to the compounds or classes of compounds disclosed in those publications. It is preferred to use compounds of low volatility, low viscosity and high reactivity. For the desired reactivity, therefore, it is generally preferred to employ compounds wherein the unsaturated carbon-carbon groups are vinyl $CH_2=CH-$, with a lesser preference for vinylidene $CH_2=C<$. Particularly preferred are acrylates and methacrylates; however as methacrylates tend to be less active than the corresponding acrylates, they preferably form only a small proportion of the diluent where they are used.

The monofunctional material may comprise a single monomer or a mixture of monomers. Straight chain acrylates of lower alcohols (e.g. C_{1-4} alcohols) tend to be too volatile and therefore should form only a small proportion of the reactive liquid material or be avoided. Acrylates of branched chain alcohols e.g. isodecyl alcohol are less volatile but more preferred are acrylates of cyclic or polycyclic alkanols, e.g. tetrahydrofurfuryl acrylate and isobornyl acrylate. Examples of the monofunctional

acrylates that may be used include long chain aliphatic acrylates e.g. wherein the aliphatic group contains at least 8, preferably at least 10 carbon atoms, such as lauryl acrylate and stearyl acrylate, and acrylates of alkoxylated alcohols e.g. 2-(2-ethoxyethoxy)ethyl acrylate. The monofunctional material need not necessarily be an acrylate; for example N-vinyl-2-pyrrolidone may be used. Further examples of monofunctional monomers are Sartomer CD 9050 (a monofunctional acid ester) and Sartomer CD 611 (an ethoxylated tetrahydrofuran acrylate).

So that the desired amounts of polyfunctional material may be incorporated into the ink, the overall viscosity of the monofunctional material of the diluent preferably is as low as possible, e.g. 20 mPa.s or less, more preferably 16 mPa.s or less, at 30°C.

The difunctional material, which may comprise a single monomer or mixture of monomers, preferably has a viscosity not greater than 30mPa.s, and preferably not greater than 20 mPa.s, at 30°C. Preferred components are diacrylates of glycols and polyglycols, especially propylene glycol and polypropylene glycols e.g. di-, tri- and higher propylene glycols. Di- acrylates of tri- or higher hydric alcohols may also be used. Examples of such diacrylates having a viscosity at 30°C of not greater than 20 mPa.s are the diacrylates of 1,4-butanediol, neopentylglycol, propoxylated neopentyl glycol, diethylene glycol,

hexanediol, dipropylene glycol, tripropylene glycol, triethylene glycol and polyethylene glycols.

The tri- or higher functional material may also comprise a single monomer or a mixture of monomers. Alkoxylated acrylates such as those obtained by acrylating the products of ethoxylating or propoxylating an initiator containing three or more active hydrogen atoms are particularly preferred. Examples of initiators having three or more active hydrogen atoms include glycerol, trimethylol propane, pentaerythritol and neopentyl alcohol. Examples of such alkoxylated acrylates are ethoxylated trimethylol propane triacrylates, propoxylated glyceryl triacrylates, Sartomer SR 9008 (an alkoxylated trifunctional acrylate ester) and propoxylated pentaerythritol tetraacrylates. Other examples of tri- or higher functional monomers are tris (2 - hydroxyethyl) isocyanurate triacrylate, and Sartomer SR 9012 (a trifunctional acrylate ester). Preferably compounds having relatively low viscosities, e.g. 200 mPa.s or less at 30°C, are chosen so that amounts towards the upper end of the range of 10 to 30% by weight, may be employed in the diluent.

While compounds having a functionality higher than 3 may also be used, they should be included at most in only small amounts, the maximum tolerable amount being less as the functionality of the compound increases. This is because as the functionality increases, so does the crosslink

as the functionality increases, so does the crosslink density in the cured product unless the molecular weight of the compound is increased but increase in molecular weight tends to lead to an increase in the viscosity of the compound.

As indicated above, the reactive liquid material must also include at least one oligomer containing unsaturated carbon-carbon bonds polymerisable by radiation. Preferably, the oligomeric component of the reactive liquid material, which may comprise one or more oligomers, has a functionality greater than 1 and thus consists of a component having, or mixture of components at least one of which has, at least two unsaturated carbon-carbon bonds polymerisable by radiation. More preferably the functionality of the oligomeric component is greater than 2. The equivalent weight of each oligomer is preferably at least 180, more preferably at least 200 or 220. However, in general, increase in equivalent weight is accompanied by increase in viscosity, thus restricting the amount of the oligomer that may be included in the composition. Preferably therefore, the equivalent weight does not exceed 750 and more preferably does not exceed 500.

As in the case of the other reactive components, oligomers which are polyacrylates are preferred because of their relatively low viscosity compared with other oligomeric polyfunctional materials. Examples include the

polyfunctional products of acrylating hydroxy-terminated polyesters, known as polyester acrylates, the polyfunctional products of acrylating urethane oligomers, known simply as urethane acrylates, and epoxy acrylates. Alkoxylated acrylates are not regarded as oligomers.

It appears that there is an optimum concentration for the oligomeric material beyond which the improvement in properties is marginal. Since increasing the concentration tends to increase viscosity, it is generally not desirable to employ more than this optimum amount which will vary according to the choice of the oligomeric material and of the other components of the reactive liquid material. In general, this optimum will not exceed 30%, of the reactive liquid material and will generally be not more than 25% e.g. 10 to 22%, more generally 15 to 20%, by weight of the total amount of reactive liquid material in the ink.

The reactive liquid material should be essentially of low volatility and preferably substantially non-volatile at ambient temperatures and preferably also at the printhead temperature if above ambient.

A silicone derivative containing at least one radiation-polymerisable carbon-carbon unsaturation is a preferred component of the ink composition for reducing its surface tension, especially when the ink is intended for printing on plastics with low surface tension surfaces e.g.

polyolefins and ABS. Preferably, it is employed in amount to give a surface tension below 35 dynes/cm and generally in the range 25 to 35 dynes/cm. In general, the silicone derivative will be used in amounts of 0.05-0.15 to 1-3% by weight, depending on the molecular weight of the derivative, more preferably 0.1 to 0.6% by weight of the ink. The inclusion of the silicone derivative in such quantities also reduces the tendency to blocking of sheets printed with the ink and improves dot definition. While greater amounts may further reduce surface tension, other properties are likely to be adversely affected. Examples of suitable compounds are silicone acrylates e.g. acrylates of organo modified silicones, for example organo modified polysiloxanes e.g. comprising repeating units of

the structure $-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{\mathrm{Si}}}-\mathrm{O}-$ where each R is a monovalent hydrocarbyl group, e.g. methyl or phenyl, and at least one unit of the structure $-\underset{\underset{X}{|}}{\overset{\overset{R}{|}}{\mathrm{Si}}}-\mathrm{O}-$ where R is as defined above and X contains an acrylate (CH_2-CH.COO-) group. In one preferred embodiment, the acrylate group is connected to the silicon atom via an alkoxy or polyalkoxy group. Preferably the chosen silicone derivative will have one or two radiation-polymerisable unsaturated carbon-carbon bonds. While the silicone component is deemed to be part of the reactive liquid material of the composition, as the amount of the silicone derivative used in the composition is relatively small, it may be ignored when calculating relative amounts of mono-, di- and/or tri- or higher functional material in the reactive liquid material.

As stated above, it is preferred that the reactive liquid material contains monofunctional, difunctional and tri- or higher functional components. The total amount of monofunctional material in the ink (including monofunctional oligomer if present) will generally form at least 20%, e.g. from 20 to 60% by weight, preferably from 20 to 50% by weight, and more preferably from 40 to 50% by weight of the total reactive material in the ink. If less than about 20% is employed, the viscosity of the ink may be

too high for some purposes. If, on the other hand, the amount significantly exceeds 60%, the properties of the print, and in particular abrasion resistance and hardness may suffer, and also the rate and/or degree of cure of the ink may be reduced.

The balance of polyfunctional material in the reactive liquid diluent is preferably made up of both difunctional and tri- or higher functional components. The total amount of difunctional material (including difunctional oligomer, if present) is preferably at least 5% by weight of the total amount of reactive material in the ink. To achieve the desired combination of viscosity of the ink and flexibility of the print derived therefrom, preferably the difunctional material is present in an amount in the range 10 to 35% by weight of the total amount of reactive material in the ink, more preferably 17½ to 30% by weight, and most preferably 20 to 30% by weight.

The total amount of tri- or higher functional material in the ink (including tri- or higher functional oligomer; if present) is preferably greater than 10 but not more than 30% by weight of the total amount of reactive liquid material in the ink. Preferably it is present in an amount of at least 15% by weight and more preferably from 20 to 30% by weight. If used in an amount of less than 10% by weight, the properties of the print obtained from the ink, and in particular hardness and scratch resistance, may tend to suffer. On the other hand, if used in amounts of more

than about 30% by weight, the viscosity of the ink tends to be too high and the print may become unacceptably brittle and inflexible.

It is preferred that the total of di- and higher functional material in the ink forms at least 35% of the total of reactive material in the ink.

A feature that is relevant to the control of the properties of the print derived from the ink, and in particular its physical properties such as hardness, abrasion resistance, modulus, flexibility and elasticity, is the overall functionality of the reactive material in the ink; i.e. the average number of radiation polymerisable unsaturated carbon-carbon bonds per molecule. If this value is too low, the print will be too soft but if it is too high, the print will tend to be brittle and to craze or crack when the substrate on which it has been printed is non-absorbent, e.g. as in a plastic substrate, and is flexed. Preferably, the amounts of mono-, di- and tri- and higher functional components of the ink are selected such that this value will be in the range 1.25 to 2, more preferably 1.25 to 1.85, most preferably 1.3 to 1.7..

While inks according to the invention may be formulated for curing by any suitable form of electromagnetic radiation, visible light or, more preferably, ultra-violet light is preferred and for this purpose the ink will also preferably

include at least one photoinitiator. Conventional photoinitiators may be employed and the choice will depend upon the choice of colorant and the wave length of the radiation. Examples of suitable photoinitiators are:

2,2-dimethyl-2-hydroxy-acetophenone,
1-hydroxy-1-cyclohexyl-phenyl ketone,
2,2-dimethoxy-2-phenylacetophenone,
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one,
2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one,
2,4,6-trimethylbenzyl-diphenyl-phosphine oxide,
1-chloro-4-propoxythioxanthone,
Isopropyl thioxanthone (mixture of 2- and 4- isomers),
Benzophenone,
Blends of bis (2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide and 1-phenyl-2-hydroxy-2-methyl propanone,
Blends of bis (2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide and 1-hydroxy-cyclohexyl-phenyl ketone,
bis (2,4,6-trimethylbenzoyl)phenylphosphine oxide, and
Camphorquinone.

In order to obviate, so far as possible, the obscuring effect of the colorant, especially where this is a pigment, a mixture of photoinitiators is preferably used whose peak

energy absorbtion levels are at different wave lengths within the range of the selected radiation. In the inks of the present invention, preferential absorption of incident UV radiation by the pigments leads to depletion of the available energy for the photoinitiator(s). This can place considerable constraints on the cure speed and level of conversion achievable especially with black pigmented ink formulations. It is therefore preferred to employ photoinitiator blends which are sensitive to the wavelengths not absorbed, or only partially affected, by the pigments. Typically this "absorption window" is between 350-400nm.

The initiators will generally be used in amounts of from about 3 to about 15% more usually about 5 to about 10% by weight of the ink.

Activators, e.g. co-initiators or amine synergists, for the photoinitiators may also be included, if desired. Examples include ethyl-4-(dimethylamino)benzoate, 2-ethylhexyl dimethylaminobenzoate, and dimethylaminoethyl methacrylate.

In operation, the ink is ejected from an ink jet printer and exposed to the selected radiation during its flight from the printhead to the substrate to be printed or, more preferably after deposition on the substrate. Generally speaking, the smaller the throw distance, that is the distance from the printhead to the substrate, the better

the print quality. However it is preferably no less than 0.5 mm and even at distances of 1.5 mm or 2 mm or even higher, acceptable results may be obtained. For most applications, the preferred throw distance will be in the range 0.5 to 0.75 mm. Curing of the ink is aided by the absence of oxygen and thus it is preferred to provide an inert gas atmosphere, e.g. nitrogen over the substrate in the zone where the ink is exposed to the radiation. Curing is preferably effected using radiation in the UVA and near-visible frequencies.

Inks according to the invention may be formulated for use in any of the available kinds of continuous and drop-on-demand ink jet printers although in general they may not be suitable for use in apparatus which employs thermal means of droplet generation. In a continuous ink jet printer, for example, former kind, for example, ink droplets which are produced continuously may be passed through a charging area where individual droplets receive an electrical charge in response to a signal and are directed towards a substrate to be printed. The droplets then pass through an electrical field causing them to be deflected by an amount which is dependent on the intensity of the charge and the field. Droplets not required to form print on the substrate may be directed to a by-pass gutter. For inks of the present invention to be suitable for use in such printers, they are preferably conductive and it may therefore be necessary to include a suitable conducting

additive. Drop-on-demand ink jet printers may be of the kind using an electrostatically accelerated ink jet or droplet sequences ejected by pressure impulse actuation, e.g. when each droplet is individually ejected from a nozzle by means of pressure pulses induced e.g. by means of a piezoelectric actuator acting on the ink in the channel supplying the nozzle.

The diluent, pigment(s), dispersant(s) (where present), dispersant synergist(s) (where present), photoinitiator(s) including activator(s) therefor (where present), and conducting additive (where present) will normally form at least 99% of the composition and preferably substantially the entire composition. As indicated above, preferably at least 99.5% by weight of the diluent is reactive liquid material.

The inks may be employed for printing on to a wide variety of substrates, both absorbent and non-absorbent including paper, glass, plastic and metal, e.g. steel, copper and aluminium, but are particularly suitable for printing on to plastics to provide a strongly bonded print of good definition and optical density, especially if the surface to be printed is pre-treated e.g. by flame, plasma etch or corona treatment to raise the surface energy. Preferably the surface energy should be at least about 36 dynes/cm and more preferably from 42 to 48 dynes/cm.

Examples of plastics on which the inks of the present invention have been successfully printed are polyolefins such as polyethylene (including high density polyethylene) and polypropylene, vinyl chloride polymers, ABS and foamed plastics such as expanded polystyrene.

The invention is now illustrated but in no way limited by the following Examples, in which all parts are expressed as parts by weight except where otherwise indicated.

Example 1

The compositions set out in Table 1 below were formulated into inks in the manner now described.

Preparation of Millbase

The pigment was ground, with the appropriate amount of hyperdispersant to ensure minimum millbase viscosity, using conventional bead milling techniques. The millbase so formed was processed until a fine particle dispersion was obtained. The particle grind was assessed by visual microscopy and a filterability test. The finished millbase was removed from the grinding media using an appropriately sized mesh either by pressure or gravity.

Preparation of Ink from Millbase

All the following blending operations were carried out in opaque vessels (either amber glass or stainless steel)

using an electrically operated high speed mixer fitted with a stainless steel rotor blade. A homogenous mixture was formed of the reactive diluent(s) and oligomers. The photoinitiator(s), either in solid or liquid form, were then added and stirring/heating continued until all insoluble components dissolved. The millbase was then carefully added to the stirred/heated vehicle in a manner to avoid any unwanted 'shock' crystal seeding/growth. Finally, the silicone polyether acrylate was added and stirring/heating continued until visual homogeneity was achieved.

The ink composition so formed was filtered using a proprietary cartridge filter rated at 1 micron absolute filter rating. Following bottling a retained sample was analysed for viscosity, visual appearance, cure rate, surface tension and ageing at elevated temperature (60°C).

The viscosities of the ink compositions were all in the range 15-20cps measured using a Brookfield Viscometer at 30°C and their values for surface tension were all in the range of 26-28 dynes/cm.

The inks were used to form coloured print on moulded ABS cards using a 128 channel greyscale drop-on-demand printhead of the kind described for example in EP-A-0.277.703 and EP-A-0.278.590 with a nozzle diameter of 25μm and a distance of 2mm between the printhead and the card.

Curing was by means of a Fusion F300s UV Lamp with a 152mm (6 inch) long "D bulb" at 11.8 w/mm (300w/inch) using cure energies in the range 1-3J/cm^2. Curing was complete within one second.

The print was well defined with acceptable colour density. The cyan, magenta and black inks all exhibited colour densities greater than 1.5 and were typically about 1.8. The colour density of the yellow ink was greater than 1, typically 1.1.

The print exhibited good adhesion to the card and good scratch resistance. Scratching with a fingernail did not remove the print and on further testing of adhesion by scoring and crosslinking the print with a scalpel and attempting to remove it by applying Sellotape to the scored surface and then peeling off the Sellotape, no detectable removal of ink was observed. The hardness of the print was assessed in conventional manner using pencils of different hardnesses. The hardness is determined as the lowest hardness value to form a scratch on the print. Print formed from the inks of the present invention generally exhibited hardnesses of 6H-7H.

The print remained unaffected when the card was subjected to the dynamic bending stress test in accordance with International Standard ISO/IEC 10 372.

TABLE 1

	BLACK	CYAN	MAGENTA	YELLOW	CYAN	MAGENTA
ACTILANE 430	10%	15.00%	10%	10%	10%	10%
ACTILANE 251	15%	15.00%	15%	15%	15%	15%
TEGORAD 2200	0.40%	0.40%	0.40%	0.40%	0.40%	0.40%
ISOBORNYL ACRYLATE	39.70%	40.00%	38.35%	41.48%	40.85%	41.47%
SARTOMER 306	23.00%	22.90%	23.00%	22.0%	23.67%	23.00%
SPEEDCURE ITX	2.00%	-	-	-	-	-
QUANTACURE EHA	3%	-	-	-	-	-
IRGACURE 907	●.03%	-	-	-	-	-
REGAL 250R	1.50%	-	-	-	-	-
SOLSPERSE 24000	0.38%	0.60%	0.75%	0.30%	0.03%	5.0●%
SOLSPERSE 5000	0.03%	0.11%	-	-	0.01%	-
IRGALITE BLUE GLVO	-	1.00%	-	-	0.05%	-
HOSTAPERM RED	-	-	2.50%	-	-	0.10%
PALIOTOL YELLOW	-	-	-	0.75%	-	-
SOLSPERSE 22000	-	-	-	0.07%	-	-
LUCERIN TPO	-	●.40%	5.00%	5.00%	5.00%	5.00%
DAROCURE 1173	-	●.40%	5.00%	5.00%	5.00%	5.00%
SPEEDCURE EDB	-	-	-	-	-	-
IRGACURE 369	-	-	-	-	-	-

KEY:

Actilane 430 - trimethylpropane ethoxylate triacrylate (ex Akcros)
Actilane 251 - trifunctional urethane acrylate prepolymer (ex Akcros)
TegoRad 2200 - silicone polyether acrylate (ex Tego Chemie Service)
Isobornyl acrylate (Ex Cray Valley Products)
Sartomer 306 - tripropylene glycol diacrylate (ex Cray Valley Products)
Speedcure ITX - isopropylthioxanthone (ex Lambsons)
Speedcure EDB - ethyl 4-(dimethylamino)benzoate (ex Lambsons)
Irgacure 369 -2-benzyl-2-diethylamino-1-(4-

morpholinophenyl)-butanone-1
Solsperse 5000/22000/24000 - hyperdispersants (ex Zeneca)
Regal 250R - carbon black, C.I. pigment black 7 (ex Cabot)
Irgalite Blue GLVO - copper phthalocyanine, C.I, pigment blue 15:4 - (ex Ciba Geigy)
Hostaperm Red E5B 02 - quinacridone, C.I. pigment violet 19 - (ex Hoechst)
Paliotol Yellow - isoindoline, C.I. pigment yellow 185 - (ex BASF)
Quantacure EHA -2-ethylhexyl p-dimethylaminobenzoate (ex Great Lakes)
Irgacure 907 - 2-methyl-1-(4-methylthio)phenyl-2-morpholino-propan-1-one (ex Ciba Geigy)
Darocure 1173 - 1-phenyl-2-hydroxy-2-methylpropane (ex Merck)
Lucirin TPO - 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (ex BASF).

The functionality of the reactive material of each of the above formulations was approximately 1.5.

Example 2

In the same manner as Example 1, a further series of ink jet ink formulations were prepared having the compositions set out in Table 2 below. Coloured print was formed from the inks in the manner described in Example 1 and similar results were obtained.

TABLE 2

	ORANGE	VIOLET	GREEN
ACTILANE 430	15%	9.55%	10%
ACTILANE 251	15%	14.32%	15%
TEGORAD 2200	0.40%	0.38%	0.40%
ISOBORNYL ACRYLATE	39%	21.41%	38.8%
N-VINYL PYRROLIDONE	-	19.09%	-
SARTOMER 306	23%	23.37%	23%
SPEEDCURE ITX	-	-	-
QUANTACURE EHA	-	-	-
IRGACURE 907	-	-	-
REGAL 250R	-	-	-
SOLSPERSE 24000	0.6%	0.535%	0.64%
SOLSPERSE 5000	-	0.135%	0.16%
CROMOPHTHAL ORANGE GP	2%	-	-
CROMOPHTHAL VIOLET B	-	1.67%	-
MONASTRAL GNX-X	-	-	2%
SOLSPERSE 22000	-	-	-
LUCERIN TPO	5%	4.77%	5%
DAROCURE 1173	5%	4.77%	5%
SPEEDCURE EDB	-	-	-
IRGACURE 369	-	-	-

Example 3

In the same manner as described in Example 1, a further series of ink jet ink formulations were prepared having the compositions set out in Table 3.

Coloured print was formed from the inks in the manner described in Example 1 and similar results were obtained.

TABLE 3

	BLACK	CYAN	MAGENTA	YELLOW
ACTILANE 430	12.50%	12.50%	12.50%	12.50%
ACTILANE 251	12.50%	12.50%	12.50%	12.50%
TEGORAD 2200	5.00%	0.40%	0.40%	0.40%
SARTOMER 506*	39.70%	40.00%	38.35%	41.48%
SARTOMER 306	23.00%	22.90%	23.00%	22.0%
SPEEDCURE ITX	2.00%	-	-	-
QUANTACURE EHA	3.00%	-	-	-
IRGACURE 907	5.00%	-	-	-
REGAL 250R	1.50%	-	-	-
SOLSPERSE 24000	0.38%	5.00%	0.75%	0.30%
SOLSPERSE 5000	0.03%	0.11%	-	-
IRGALITE BLUE GLVO	-	1.00%	-	-
HOSTAPERM RED E5B 02	-	-	2.50%	-
PALIOTOL YELLOW D1155	-	-	-	0.75%
SOLSPERSE 22000	-	-	-	0.07%
LUCERIN TPO	-	5.00%	5.00%	5.00%
DAROCURE 1173	-	5.00%	5.00%	5.00%

* Sartomer 506 is isobornyl acrylate (ex Cray Valley Products)

Example 4

In a series of further experiments it was found that incrementally replacing the Actilane 251 by Actilane 430 reduced the scratch resistance of the resultant cured print when tested following ASTM test method D 3363-92a, although merely increasing the Actilane 430 to 14% while reducing the Actilane 251 to 11% made no apparent difference to the scratch resistance.

If the Actilane 251 is completely replaced by Actilane 430 the print derived from the composition tends to be too soft for many applications.

If the amount of Actilane 251 is increased to 25% or 30% at the expense of Actilane 430 and Sartomer 306 the viscosity tends to increase without a sufficiently concomitant beneficial increase in physical properties.

Example 5

A white ink was prepared having the following formulation:

Actilane 422	18.55%
Actilane 251	15%
N-vinyl pyrrolidone	20%
Solsperse 24000	1.05%
Tegorad 2200	0.4%
Irgacure 907	10%
White pigment	35%

Actilane 422 is dipropylene glycol diacrylate (ex Akcros). The white pigment is Tioxide TR92.

White print was formed from the ink in the manner described in Example 1 and similar results were obtained.

CLAIMS:

1. A radiation curable ink jet ink having a viscosity not greater than 35 mPa.s at 30°C as measured using a Brookfield Viscometer fitted with a small sample adaptor having a No. 18 spindle and a rotational speed of 60 rpm, giving a shear rate of 79.2 sec^{-1}, and comprising a colorant component, a diluent consisting essentially of reactive liquid material and, optionally, at least one photopolymerisation catalyst and wherein the reactive liquid material is formed of both monofunctional and polyfunctional material and comprises 5 to 30% by weight of at least one oligomer.

2. An ink jet ink as claimed in claim 1 characterised in that said at least one oligomer has a functionality greater than 1.

3. An ink jet ink as claimed in claim 2 characterised in that said at least one oligomer has a functionality greater than 2.

4. An ink jet ink as claimed in claim 2 or claim 3 characterised in that said at least one oligomer is selected from polyester acrylates, urethane acrylates and epoxy acrylates.

5. An ink jet ink as claimed in any one of claims 2 to 4 characterised in that said at least one oligomer forms not more than 25% by weight of the reactive liquid material.

6. An ink jet ink as claimed in any one of claims 2 to 4 characterised in that said at least one oligomer forms from 10 to

22% by weight of the reactive liquid material.

7. An ink jet ink as claimed in any one of claims 1 to 6 further including a silicone derivative containing carbon-carbon unsaturation which is polymerisable by radiation.

8. An ink jet ink as claimed in claim 7 characterised in that the silicone derivative is selected from silicone acrylates.

9. An ink jet ink as claimed in claim 7 or claim 8 characterised in that the silicone derivative contains repeating units have the structure

$$\begin{array}{c} R \\ | \\ -\ Si\ -\ O\ - \\ | \\ R \end{array}$$

and at least one unit the having the structure

$$\begin{array}{c} R \\ | \\ -\ Si\ -\ O\ - \\ | \\ X \end{array}$$

where each R is monovalent hydrocarbyl and X contains an acrylate group.

10. An ink jet ink as claimed in claim 5 characterised in that R is methyl.

11. An ink jet ink as claimed in any one of claims 7 to 10 characterised in that the silicone derivative is employed in an amount such that the ink has a surface tension of 25 to 35 dynes/cm.

12. An ink jet ink as claimed in any one of claims 7 to 11 characterised in that the silicone derivative forms from 0.05 to 1% by weight of the ink.

13. An ink jet ink as claimed in any one of the preceding claims characterised in that the colorant comprises a pigment dispersed in the reactive diluent.

14. An ink jet ink as claimed in claim 13 further including a dispersant for the pigment.

15. An ink jet ink as claimed in any one of the preceding claims characterised in that the colorant forms from 0.01 to 50% by weight of the ink.

16. An ink jet ink as claimed in any one of the preceding claims characterised in that the colorant forms from 0.1 to 10% by weight of the ink.

17. An ink jet ink as claimed in any one of the preceding claims characterised in that said reactive liquid material comprises monofunctional, difunctional and tri- or higher functional components.

18. An ink jet ink as claimed in any one of the preceding claims characterised in that the components of the reactive liquid material are selected from acrylates, methacrylates and N-vinyl pyrrolidone.

19. An ink jet ink as claimed in any one of the preceding claims characterised in that the viscosity of the monofunctional material of the reactive diluent is not greater than 20 mPa.s at 30°C.

20. An ink jet ink as claimed in any one of the preceding claims characterised in that the monofunctional material of the diluent comprises at least one monomer selected from long chain aliphatic acrylates, acrylates of branched chain alcohols, acrylates of alkoxylated alcohols, acrylates of cyclic and polycyclic alkanols, and N-vinyl pyrrolidone.

21. An ink jet ink as claimed in claim 19 or claim 20 in which the monofunctional material comprises isobornyl acrylate.

22. An ink jet ink as claimed in any one of the preceding claims characterised in that the reactive diluent includes difunctional material and said difunctional material has a viscosity of not greater than 20 mPa.s at 30°C.

23. An ink jet ink as claimed in any one of the preceding claims characterised in that the reactive diluent includes difunctional material and said difunctional material comprises at least one monomer selected from diacrylates of glycols and polyglycols.

24. An ink jet ink as claimed in claim 23 characterised in that the difunctional material of the reactive diluent comprises at least one monomer selected from the diacrylates of 1,4-butanediol, neopentyl glycol, propoxylated neopentyl glycol, hexanediol, dipropylene

glycol, tripropylene glycol, diethylene glycol, triethylene glycol and polyethylene glycols.

25. An ink jet ink as claimed in any one of the preceding claims characterised in that the reactive diluent includes tri- or higher functional material and said tri- or higher functional material comprises at least one monomer selected from ethoxylated trimethylol propane acrylates and propoxylated glyceryl acrylates.

26. An ink jet ink as claimed in any one of the preceding claims characterised in that the monofunctional material forms at least 20% by weight of the reactive liquid material.

27. An ink jet ink as claimed in any one of the preceding claims characterised in that the monofunctional material forms 20 to 60% by weight of the reactive liquid material.

28. An ink jet ink as claimed in any one of the preceding claims characterised in that monofunctional material forms not more than 50% by weight of the reactive liquid material.

29. An ink jet ink as claimed in any one of the preceding claims characterised in that the monofunctional material forms 40 to 50% by weight of the reactive liquid material.

30. An ink jet ink as claimed in any one of the preceding claims characterised in that at least 5% by weight of the reactive liquid material comprises difunctional material.

31. An ink jet ink as claimed in any one of the preceding claims characterised in that 10 to 35% by weight of the reactive liquid material comprises difunctional material.

32. An ink jet ink as claimed in any one of the preceding claims characterised in that 17½ to 35% by weight of the reactive liquid material comprises difunctional material.

33. An ink jet ink as claimed in any one of the preceding claims characterised in that 20 to 30% by weight of the reactive liquid material comprises difunctional material.

34. An ink jet ink as claimed in any one of the preceding claims characterised in that greater than 10 but not more than 30% by weight of the reactive liquid material comprises tri- or higher functional material.

35. An ink jet ink as claimed in any one of the preceding claims characterised in that from 20 to 30% by weight of the reactive liquid material comprises tri- or higher functional material.

36. An ink jet ink as claimed in any one of the preceding claims characterised in that the overall functionality of the reactive material in the ink is in the range 1.25 to 2.

37. An ink jet ink as claimed in any one of the preceding claims characterised in that the overall functionality of the reactive material in the ink is in the range 1.25 to 1.85.

38. An ink jet ink as claimed in any one of the preceding claims characterised in that the overall functionality of the reactive material in the ink is in the range 1.3 to 1.7.

39. An ink jet ink as claimed in any one of the preceding claims characterised in that it includes at least one photoinitiator and is curable by ultra-violet light.

40. An ink jet ink as claimed in claim 39 characterised in that it includes two or more photoinitiators.

41. An ink jet ink as claimed in claim 39 or 40 characterised in that said at least one photoinitiator promotes cure in the frequency range 350-400nm.

42. An ink jet ink as claimed in any one of claims 39 to 41 characterised in that said at least one photo initiator forms from 3 to 15% by weight of the ink.

43. An ink jet ink as claimed in any one of claims 39 to 41 characterised in that said at least one photo initiator forms from 5 to 10% by weight of the ink.

44. An ink jet ink as claimed in any one of the previous claims comprising diluent, colorant, and optionally one or more of dispersant, dispersant synergist, photoinitiator, activator for photoinitiator and conducting additive and wherein said diluent, colorant, dispersant, dispersant synergist, photoinitiator,

activator for photoinitiator and conducting additive form together at least 99% by weight of the composition.

45. A method of printing on a substrate comprising directing an ink as claimed in any one of claims 1 to 44 from the printhead of an ink jet printer towards a print-receiving surface of said substrate and, during its travel from the printhead to the substrate and/or after deposition on the substrate, exposing the ink to radiation to cure the ink.

46. A method as claimed in claim 45 characterised in that the ink jet printer is a drop-on-demand printer.

47. A method as claimed in claim 45 or claim 46 characterised in that the surface is plastic.

48. A method as claimed in claim 47 characterised in that the surface is ABS or polyolefin.

49. A method as claimed in claim 47 or claim 48 characterised in that the ink has a surface tension of 25-35 dynes/cm.

50. A method as claimed in any one of claims 47 to 49 characterised in that the surface is pre-treated by flame or corona treatment.

51. A method as claimed in any one of claims 45 to 50 characterised in that the distance from the printhead to the substrate is in the range 0.5 to 1.5 mm.

52. A method as claimed in any one of claims 45 to 51 characterised in that the ink is exposed to the radiation in an inert atmosphere.

53. A printed substrate having a surface carrying print comprising a cured ink composition as claimed in any one of claims 1 to 44.

54. A printed substrate as claimed in 53 characterised in that the surface is plastic.

55. A printed substrate as claimed in 54 characterised in that the surface comprises ABS or polyolefin